07 - 10 September 2009

PROCEEDINGS

54. IWK

Internationales Wissenschaftliches Kolloquium
International Scientific Colloquium

Information Technology and Electrical Engineering - Devices and Systems, Materials and Technologies for the Future

Faculty of Electrical Engineering and Information Technology

Startseite / Index:
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TECHNISCHE UNIVERSITÄT
ILMENAU

Impressum

Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c.
Peter Scharff

Redaktion: Referat Marketing
Andrea Schneider

Fakultät für Elektrotechnik und Informationstechnik
Univ.-Prof. Dr.-Ing. Frank Berger

Redaktionsschluss: 17. August 2009

Technische Realisierung (USB-Flash-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
ilmedia
Postfach 10 05 65
98684 Ilmenau

Verlag:
Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau

ISBN (USB-Flash-Ausgabe): 978-3-938843-45-1
ISBN (Druckausgabe der Kurzfassungen): 978-3-938843-44-4

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

GAS SENSING MICROMACHINED STRUCTURE BASED ON GALLIUM ARSENIDE

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ABSTRACT

In this paper we present fabrication and electro-thermal characterization of gas sensor prepared on GaAs substrate. Surface and bulk micromachining techniques were used to obtain low power consumption microheater on suspended GaAs membrane. The microhotplate can be operated at temperatures up to 270°C and has a low d.c. power consumption of 35 mW. The thermal response of the microhotplate was lower than 5 ms measured at temperature 180°C. Gas sensing properties of device are presented on detection of low concentration ethanol vapors, where NiO sensing layer was used. The response of gas sensor increased with increasing temperature as well as response dynamic parameters.

Index Terms - GaAs suspended membrane; bulk and surface micromachining, gas sensor; NiO sensitive layer, ethanol

1. INTRODUCTION

Gas sensors based on semiconducting metal oxides are actually one of the most investigated groups of gas sensors. Sensory properties of these devices are based on change in resistance of metal oxide layer upon exposure to specific gas, where oxidation/reduction properties play a role. Resistance is measured usually by electrode structure lying below sensing layer. In spite of fact that there are many approaches [1,2] and a lot of work has been reported in this field, one can see the united effort in development of systems and microsystems compatible with the semiconductor technology used in production of integrated circuits, by means of producing microsensors and electronic circuitry on the same chip. Such circuitry can include parts for signal amplification and signal evaluation [3] and thus cost reduction can be achieved in this way. As it is well known, metal oxide gas sensors generally work in a high temperature mode to accelerate the chemical reactions between molecules of the specified gas and the surface of sensing layer [4]. However, for stable operation of integrated gas sensor system is required to keep part of substrate with electronic circuitry, except of active gas sensing area, at low temperature. Moreover, low power dissipation and thus low consumption is desired for battery-powered portable applications of sensors. All aforementioned requirements are met by micromechanical structures, where the sensing layer is placed on a suspended thin dielectric membrane prepared by a micromachining process. Typically, Si, SiO_2 or SiN membranes supported by a silicon wafer have been used as substrates [1-3]. Gallium arsenide-based MEMS devices are an attractive alternative to the well-developed silicon based MEMS. These devices have potentially significant future applications in the areas of high-speed sensor systems, in extreme temperature conditions, applications requiring radiation hardness and high-performance multi-functionality [5,6]. Furthermore the thermal conductivity of GaAs is three times lower than that of Si, and thus has a better prospect of meeting the requirement for maximum thermal resistance.

This paper includes structural and electro-thermal characterization of bulk structure gas sensor and structural and electro-thermal characterization of microheater prepared on suspended GaAs membrane.

2. DESIGN AND FABRICATION DETAILS

2.1. Fabrication of model device

The model device 'bulk' structure gas sensor was fabricated on a double side polished (100) semiinsulating GaAs substrate. The thickness of the GaAs substrates was 300 μm. The basic technological steps for the device fabrication, shown in Fig. 1, can be summarized as follow: In first step 20 nm TiN diffusion-barrier layer was deposited followed by 200 nm thin Pt layer acting as heater (Fig. 1a). The Pt simple meander was shaped by lift-off process. Next, 3 μm polyimide 2571 as an electrical insulating layer was prepared by spin-off technique and heater contact opening was made by dry etching in oxygen through PI layer (Fig. 1b). To achieve ohmic contact, contacts were covered by 20 nm Au layer. On the top of the insulating layer TiN/Pt (20 nm/200 nm) interdigited

electrodes (IDE) and bonding pads were patterned by lift-off and deposited by magnetron sputtering as for the heater (Fig. 1c). Bonding pads were covered with 20 nm thin Au layer. Finally the NiO gas sensing layer (150 nm) was deposited onto the IDE by reactive magnetron sputtering from 99.95% pure Ni target in a mixture of oxygen and argon (Fig. 1d). The distance between the Ni target and the substrate was approximately 75 mm. The apparatus was evacuated to a pressure below 5×10^{-4} Pa before deposition. A sputtering power of 600 W was used. Mass flow controllers controlled both the inert argon flow and reactive oxygen flow. The relative partial pressure of oxygen in the reactive mixture O_2–Ar was 20%. The total gas pressure was kept at 0.5 Pa. After each deposition process, whole structure was annealed at 400°C/ 1h in N_2 atmosphere for stabilization. Top view of final structure is shown on Fig. 2.

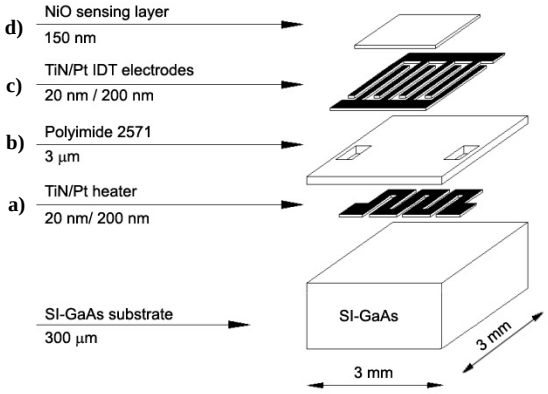

Figure 1 Process sequence of the 'bulk' gas sensor structure on SI-GaAs substrate.

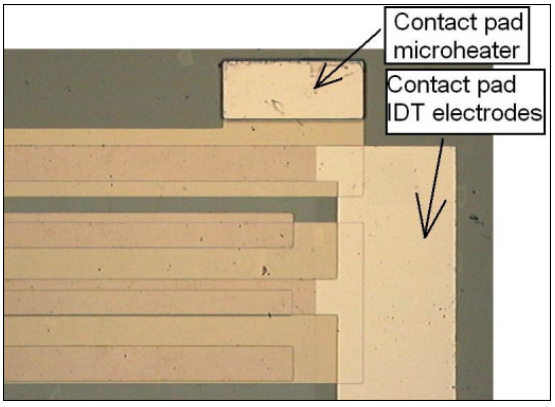

Figure 2 Top view of model device, picture taken from optical microscope

2.2. Fabrication of microheater and GaAs suspended membrane

Contrary to 'bulk' structure of GaAs based gas sensor, microheater was prepared on GaAs suspended membrane on purpose to achieve low power-consumption microstructure (Fig. 3) which will be applied in future on gas microsensor. Surface and bulk micromachining by selective reactive ion etching (SRIE) based on CCl_2F_2 plasma chemistry was investigated to create GaAs suspended membrane. In our study, GaAs/AlGaAs double layer grown by MBE is used to form membrane where AlGaAs is used as etch-stop layer (Fig. 3a). As heater material, TiN/Pt double layer was used, prepared in the same way as for model device. After each deposition process, whole structure was annealed at 400°C/ 1h in N_2 atmosphere for stabilization. We used double meander for heater shape to obtain uniform heat distribution over the active area. Connection wires and contact pads are created from 200 nm Au (Fig 3b). In the same step, Ni mask on the substrate-backside was defined by double side lithography, patterned by lift-off technique.

2.2.1. Surface micromachining of GaAs layer

In the first step, photoresist AZ 5214 was used to form etching mask (Fig. 3c) and samples were etched by dry-etching in CCl_2F_2 plasma to the AlGaAs stop layer (Fig. 3d). The total working pressure in the chamber during front-side etching was 10 Pa, CCl_2F_2 flow was adjusted by mass flow controller at 30 sccm. The rf (13.56 MHz) power was kept at 150 W.

2.2.2. Bulk micromachining of GaAs substrate

Bulk micromachining is critical step in development of GaAs suspended membrane. Etching conditions have to carry out following requirements [7,8]: (a) a sufficient etch rate of GaAs substrate to the stop etch layer, at the anisotropy needed to minimize lateral undercutting, (b) a selectivity of GaAs etching to the etch mask and to the stop etch layer. We have found in our experiments the optimal etching rate for preparing 2 μm thick suspended membrane. CCl_2F_2 was used again as the process gas. For backside etching (Fig. 3e), the same conditions were used as for front-side, except working pressure, which was kept at 18 Pa. The etch rate was about 2 μm/min, the selectivity to the Ni mask better than 2000 and to the AlGaAs stop etch layer better than 1000. Afterwards, the resist was striped off and AlGaAs layer dissolved in mixture of H_3PO_4, H_2O_2 and H_2O in ratio 3:1:1 respectively. The size of the chip and prepared membrane can be seen on Fig. 3f. SEM images of top view and backside view are shown in Fig. 4.

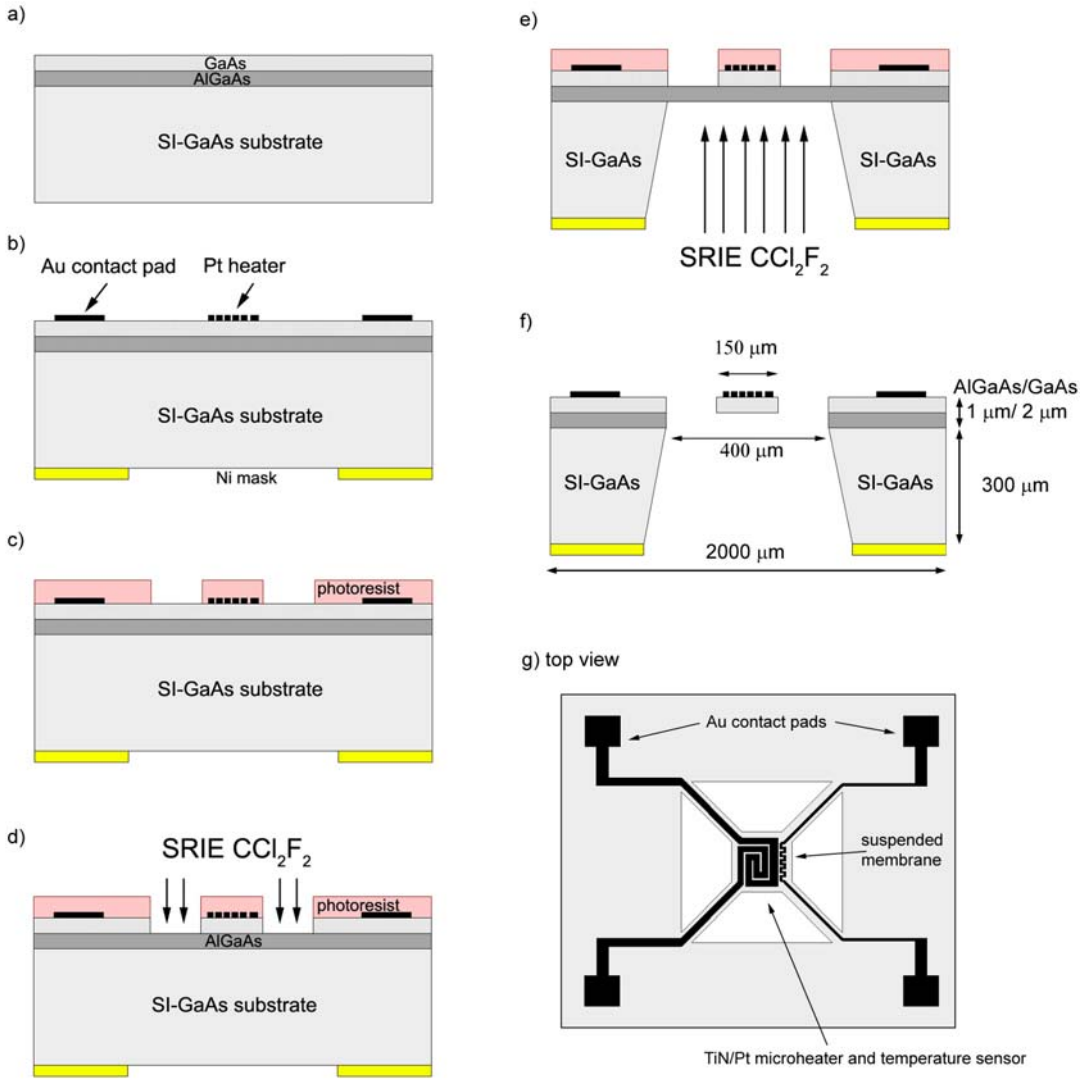

Figure 3 Cross sectional view of process steps: (a) MBE of AlGaAs/GaAs double layer, (b) deposition of Pt heater, Au contacts and Ni mask for backside etching, (c) preparation of etching mask, (d) surface micromachining, (e) bulk micromachining, (f) removing of resist and AlGaAs stop etch layer.

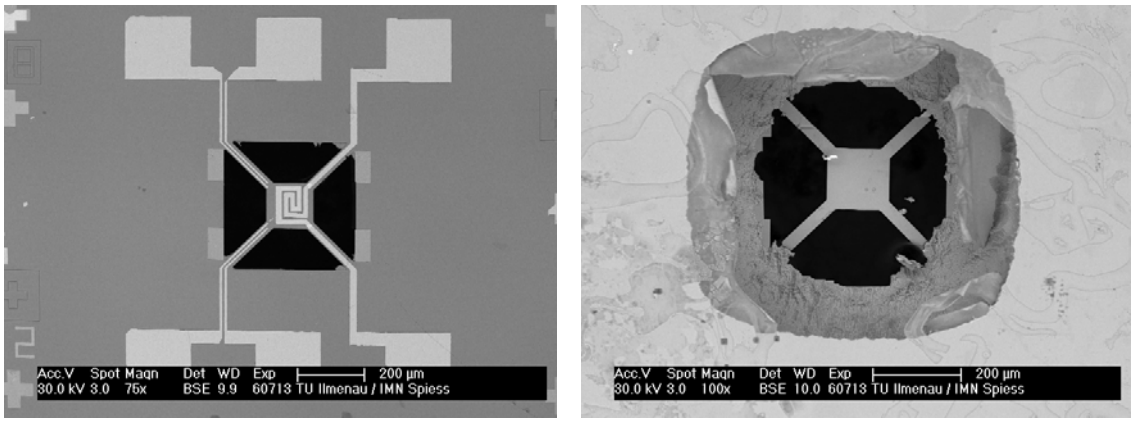

Figure 4 Suspended membrane with microheater: (a) top view and (b) backside view.

3. ELECTRO-THERMAL CHARACTERIZATION

In order to control the temperature of the heater integrated in 'bulk' structure model device and microheater prepared on suspended GaAs membrane, it is necessary to characterize the relationship between the resistance of the heater element and its operating temperature. Both structures presented in this paper were calibrated over a temperature range of ambient temperature to about 150°C in a temperature-controlled oven Eurotherm 2408. A FLUKE 45 multimeter measured the heater resistances. Heaters exhibit linear characteristics in measured temperature range and can be described by first-order function:

$$R_H(T) = R_0[1+\alpha(T-T_a)], \qquad (1)$$

where R_H is the resistance of the heater at temperature T, R_0 is the resistance at ambient temperature T_a, and α is the linear temperature coefficient of resistance (TCR). Typical characteristics are shown on Fig. 5, resistance of heater on model device at ambient temperature varied from 60 to 62Ω, for microheater on suspended membrane this value varies from 80 to 97 Ω depending on location on the whole substrate during deposition.

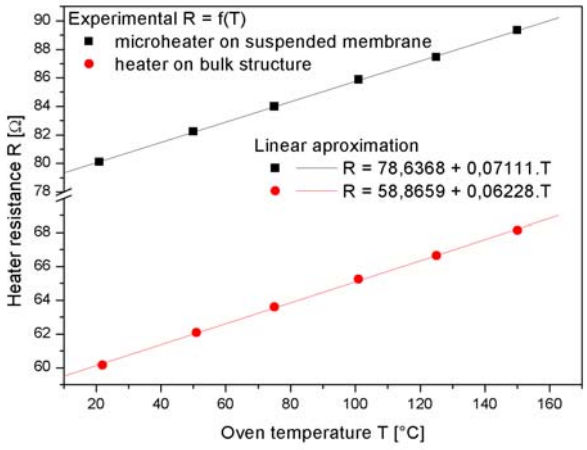

Figure 5 Calibration characteristics showing linear temperature-dependence of resistance.

Calculated TCR for heater fabricated on bulk GaAs substrate was $1{,}058\times10^{-3}$°C, slightly higher than one, obtained for microheater prepared on membrane which value was $0{,}904\times10^{-3}$°C. The difference is probably due to different surface, which was in first case polished GaAs substrate and in second case MBE grown GaAs. Due to disconnection of temperature sensor contacts during fabrication process of suspended membrane we were not able to determine temperature over the membrane with independent measurement through change in temperature sensor resistance.

Both devices were characterized by voltage-current measurement. Temperature over the active area was determined straight from the resistance of heater. Power consumption vs. temperature is shown on Fig. 6 and Fig. 7. Whereas bulk structure gas sensor exhibits power consumption of 850 mW at 200°C, consumption of microheater on membrane is only 25 mW at the same temperature.

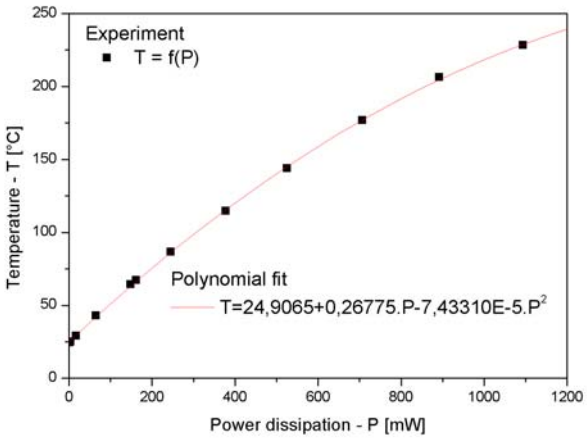

Figure 6 Temperature vs. heater power dissipation in bulk structure design gas sensor.

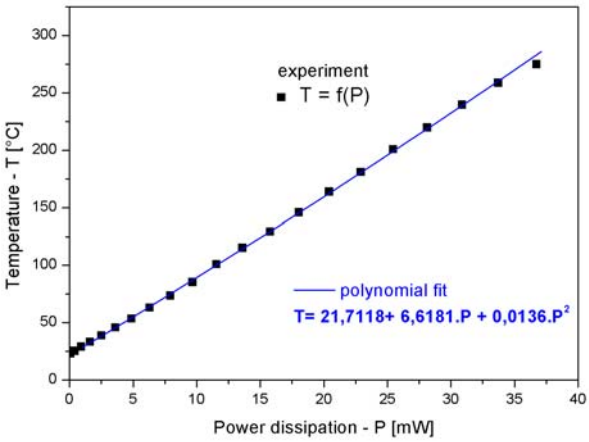

Figure 7 Temperature vs. microheater power dissipation in suspended membrane design.

As one can predict, power consumption of bulk structure is significantly higher than design with suspended membrane as the major thermal mass in second case constitute only from 2 µm thick square membrane with side of 150 µm.

3.1. Thermal time constant measurement

To minimize power consumption of heater, AC temperature modulation is promising way of how to achieve it [1,2]. Furthermore, Vegara et al pointed to new opportunities of using temperature-modulated microhotplate gas sensor for quantitative gas mixture analysis [9]. To use low frequency temperature modulating signal, it is necessary to determine maximum modulating frequency by measuring thermal time constant (TTC) of investigated device. The TTC measurement is interesting only in case of heater prepared on GaAs suspended membrane, as thermal mass of 'bulk' structure gas sensor is the whole chip and TTC of such a device is 5 min and more. In our study we used constant current source Keithley 238 to power-up the heater and Tektronix TDS305B oscilloscope to measure voltage across the heater. This voltage variation is directly linked to the change in the resistance of the heating element. The circuit was switched on by two-positional switch and oscilloscope was set-up to sense rising edge of the signal. Measured characteristics at different current flow through heater element (and so at different temperature) are shown in Fig. 8.

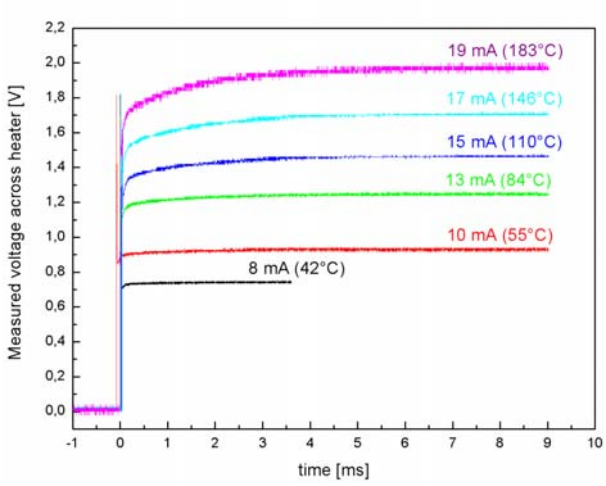

Figure 8 Measurement of voltage variation in time as function of current-flow through the heater

The TTC corresponds to the time required to reach the 99% of the steady-state voltage and was determined to be 4.2 ms when reaching the temperature of 183°C. The TTC dependence on microheater's temperature is shown in Fig. 9. One can see the rising tendency of TTC on increasing temperature. However, the higher is the temperature, and the lower is change of TTC. This effect is probably because the ratio of the thermal conductivity to heat capacity of the GaAs membrane increases with increasing temperature. However, the whole thermal losses are influenced not only by heat conduction over the membrane, but also by radiation and convection [1], which also arises with temperature and thus the TTC has rising tendency with rising temperature.

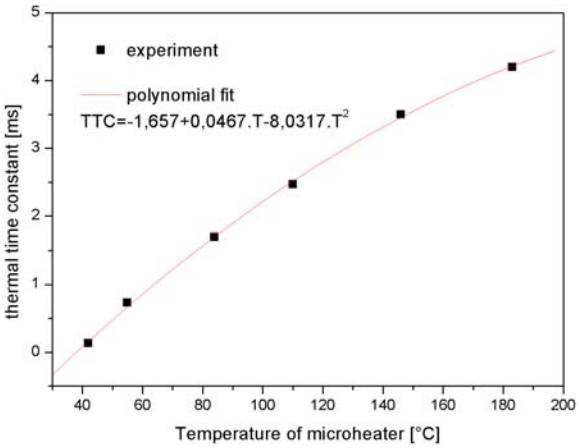

Figure 9 Thermal time constant dependence on microheater's temperature.

4. GAS SENSING TESTS TOWARDS ETHANOL

Gas sensing properties of model device with complete sensor structure was tested under exposure towards ethanol. All tests were performed in real conditions and measured relative air humidity was in range of 40-50%. Sensor was exposed in every measurement to ethanol vapor for 30 min and afterwards to air for 30 min and its response was measured through change in resistance of NiO sensing layer. Temperature of the sensor was regulated by known temperature-resistance dependence of the heater, setting resistance to desired value by powering from voltage source. Over the one cycle of measurement, operating temperature was kept on constant value. FLUKE 45 multimeter measured resistance of sensing layer. Ethanol concentration was calculated from equation 2:

$$C\,[ppm] = \frac{m_{et}}{m_{air}} \cdot \frac{M_{air}}{M_{et}} \cdot 10^6 \qquad (2)$$

where m_{et} and m_{air} stands for weight of ethanol and air respectively, in chamber and M_{et} and M_{air} stands for molar weight of ethanol and air respectively. Ethanol was evaporated from liquid phase in amount from 4 to 20 µl which corresponds to concentrations in range from 2400 ppm to 9600 ppm. Operating temperature of gas sensor was varied from 160°C to 208°C. Device was warmed up one hour before measurement to reach steady-state value of NiO resistance. This warming up process was necessary to

repeat every time the operating temperature of sensor was changed.

To check the measurement reproducibility, sensor response was measured three times at ethanol concentration of 4667 ppm at three different temperatures (165°C, 184°C, 208°C). These characteristics are shown on Fig. 10. Relative humidity (RH) of air during measurement was 41%.

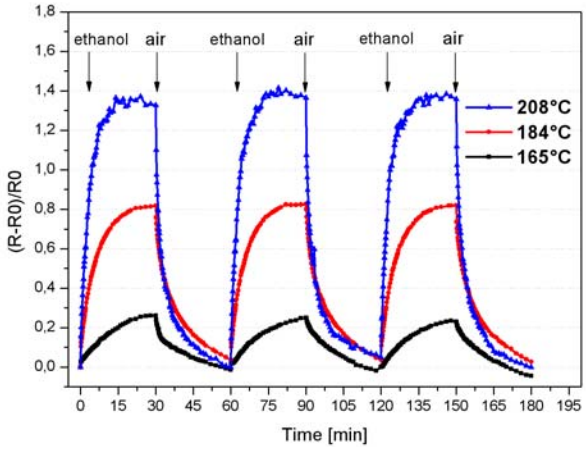

Figure 10 Response towards 4667 ppm of ethanol in air with relative humidity 41% at three temperatures.

Response was calculated as ratio (R-R0)/R0, where R is resistance of NiO layer at given time and R0 is steady state value of NiO resistance at given temperature. Response time t_r was taken at value of 70% of maximal response. Recovery time t_f was taken at 30% of minimal recovery value. As one can see from Fig. 10 and Table 1, there is minimal difference in maximal response value and measurements are fully reproducible. From Table 1 is evident, that dynamics of sensor response is improving with rising temperature. The fact that after 30 min in air after exposing sensor to gas the minimal value is different from steady-state value at beginning of measurement is probably caused by adsorption of H_2O molecules from the air. It's desorption is hard from the oxide surface, especially at relatively low operating temperatures that we used.

After these measurements, sensor was exposed towards four different ethanol concentrations at three operating temperatures. At the time of measurement, RH of air was 45 %. Characteristics are shown on Fig. 11. Maximum values of gas response were extracted and calibration curves fitted by linear functions (Fig. 12).

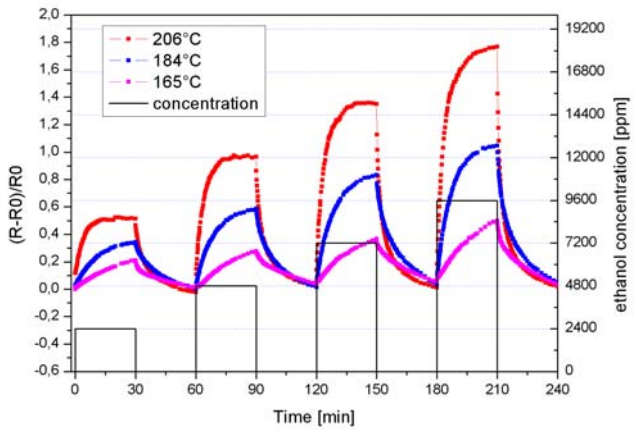

Figure 11 Response towards various concentration of ethanol where parameter is operating temperature.

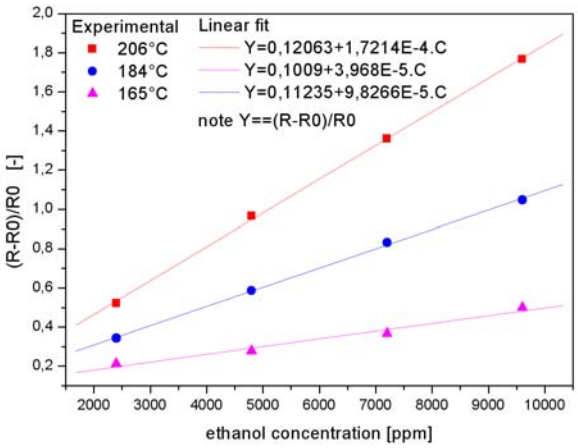

Figure 12 Calibration curves of gas sensor response for three temperatures.

From these curves it is obvious, that sensitivity towards ethanol is rising with rising operating temperature of sensor and can be calculated from equation 3:

$$S = \frac{\Delta R/R_0}{\Delta ppm}.100.10^3 \quad [\%/1000\text{ppm}], \qquad (3)$$

Summary of sensitivity values extracted from linear fitting curves is in Table 2.

Table 2 Sensitivity values towards ethanol concentration in ppm for three different temperatures.

Temperature [°C]	165	184	208
Sensitivity [%/1000ppm]	3.97	9.83	17.21

Table 1 Summary of measured response and recovery times, and maximal response value of sensor towards 4667 ppm of ethanol.

	Response time [min]			Recovery time [min]			Maximal response value [min]		
Temperature [°C]	165	184	208	165	184	208	165	184	208
1st measurement	12.8	6.8	4.2	10.5	9.0	3.7	0.26	0.82	1.37
2nd measurement	15.1	6.5	3.5	11.8	11.8	4.8	0.25	0.83	1.39
3rd measurement	13.0	6.5	3.4	10.0	8.8	4.3	0.23	0.82	1.38
Average value	13.6	6.6	3.7	10.8	9.9	4.3	0.25	0.82	1.38

5. CONCLUSIONS

In this paper we have demonstrated new approach in developing of low-power consumption micro-electromechanical structure based on GaAs low thermal conductivity suspended membrane with thickness of 2 μm. The surface and bulk micro-machining processes were developed and optimized with usage of SRIE in CCl_2F_2 plasma. Also the model device with 'bulk' structure was fabricated to ensure that material compatibility is reached and to compare a power efficiency of heating in 'bulk' structure and in structure with suspended membrane. Electro-thermal characterization was investigated on both designs and it can be concluded, that power consumption of device with microheater fabricated on suspended membrane is 34 times lower than device with 'bulk' structure, reaching the operating temperature 270°C at power consumption of 35mW.

To even more lower the power consumption by temperature modulation, it is necessary to determine maximum modulating frequency by measuring thermal time constant of investigated device. The TTC was determined to be 4.2 ms when reaching the temperature of 183°C. This means, that the highest frequency of AC modulated signal is more than 230 Hz at operating temperature of 183°C, however it should be mentioned, that highest frequency for purpose of gas sensing is not only function of TTC but one should consider the dynamics of the chemical reactions of gas species with the surface of sensing layer.

To complete the characterization of developed model device of gas sensor, its gas sensing behavior towards ethanol vapor was measured. The response dynamic parameters rose with raising temperature. From maximal response values the calibration curves were carried out and the sensitivity at three different temperatures were calculated.

In next step, the further processes on structure with heater prepared on GaAs suspended membrane will be performed to obtain low-power consumption gas sensing device.

6. ACKNOWLEDGMENT

The work was supported by Scientific Grant Agency of Ministry of Education of Slovak Republic and Slovak Academy of Sciences, No. 1/0553/09, by Science and Technology Assistance Agency under contract No. VVCE-0049-07 and No. APVV-0655-07 and PPP Programme project DAAD No. D/08/07742.

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